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Short communication

A procedure for calibration of differential scanning calorimeters

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ABSTRACT

A new approach to calibration of differential scanning calorimeters based on the difference in heat capacities of heavy and light water is described. The advantages of heavy water over salt solutions currently used for the same purpose are described. Sources of uncertainties in measurements and possible ways to reduce these are discussed.

1. Introduction

Differential scanning calorimetry (DSC) of solutions [1–3] is a method allowing determination of the enthalpies of conformational changes and phase transitions in solutions of polymers and biopolymers, and formation and decomposition of complexes in the liquid phase. DSC is also a very simple way to measure the isobaric heat capacities of liquids and solutions over a broad range of temperatures in a single experiment.

A very high precision of the measured values of heat capacities is required to determine accurately the partial molar heat capacities of dissolved proteins, which reflect the changes in protein structure with temperature and upon unfolding, especially at low concentrations. The same is true for the partial or apparent heat capacities of any solutes in dilute solutions. However, it is impossible to make the sample and reference cells identical and fill with exactly equal volumes of liquid. Introduction of a temperature-dependent calibration coefficient related to the difference in the volumetric heat capacities of the cells filled with standard samples can reduce the error of measured heat capacity and enthalpy values.

A previously suggested calibration procedure for a twin, fixed-cell, temperature-scanning calorimeter [4,5] is based on measuring the difference in heat capacities of 1 M NaCl and pure water. The present work suggests using heavy water (D_2O) in one cell and pure light water (H_2O) in the other. The difference in heat capacities is larger than for 1 M or even 6 M NaCl, which reduces the relative error of the calibration coefficient. There is no need to prepare a solution with exact concentration. There is no risk of changing concentration during degassing of the samples or adsorption and crystallization of the salt. A minimum requirement for calibration is only 1 ml of pure D_2O. Choosing another pure liquid for calibration is difficult because the difference in volumetric heat capacities between water and other pure liquids is too large and the signal goes off scale at usual scanning rates.

2. Experimental

The calorimeter was a TA Instruments NanoDSC with two 300 μl capillary cells. Water was distilled, deionized, and degassed while stirring under vacuum. The measured resistance at 298 K was 18.2 MOhm cm. Heavy water purchased from Prikladnaya himiya was degassed while stirring under vacuum. Infrared spectrum shows the light water content is less than 0.1% (determined using the dependence of absorption at 3400 cm^{-1} corresponding to O—H stretching vibrations on addition of small portions of light water).

DSC curves for the sample pairs H_2O (cell1)–H_2O (cell 2), D_2O–H_2O, H_2O–D_2O, and D_2O–D_2O were recorded at constant pressure 3.5 bar in the temperature range 278.15–393.15 K repeating the heating and cooling cycle 4 times for each pair of samples. The scanning rate was 1 K min^{-1}. The cells were cleaned with Contrad 70 solution before the experiments, and a balance scan with both cells filled with H_2O was done. The experiment was repeated 2 more times with the new samples. After that, the same procedures were repeated at a scanning rate of 2 K min^{-1}.

To remove the initial part of the curve corresponding to non-steady heating or cooling, the DSC curves were truncated; the

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